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Review Meeting of MED POL monitoring activities and the use of indicators

Athens, 12-14 December 2007

Eutrophication Monitoring Strategy for the MED POL
(REVISION)

UNEP/MAP
Athens, 2007

1. Background

After the approval of the MED POL Eutrophication Monitoring Strategy by the MED POL National Coordinators (San Gemini, May 2003), pilot monitoring programmes were formulated for three different site typologies (UNEP(DEC)/MED WG.231/14), (a) affected coastal areas, (b) areas with intense aquaculture activities and (c) coastal lagoons under eutrophication threat.

As a short-term strategy it was agreed to monitor the parameters below supporting the adoption of the TRIX index and to introduce biological monitoring in the medium and long run.

Mandatory parameters to be monitored by each country

Temperature (°C)	**Dissolved oxygen (mg/L, %*)**
pH	**Chlorophyll "a" (µg/L*)**
Transparency	**Total Nitrogen (N µmol/L)#**
Salinity (psu)	**Nitrate (NO_3-N µmol/L, µg/L*)**
Orthophosphate (PO_4-P µmol/L, µg/L*)	**Ammonium (NH_4-N µmol/L, µg/L*)**
Total phosphorus (P µmol/L, µg/L#)	**Nitrite (NO_2-N µmol/L, µg/L*)**
Silicate (SiO_2 µmol/L)	**Phytoplankton (total abundance, abundance of major groups, bloom dominance)**

not mandatory, only recommended due to methodological difficulties
* units supporting TRIX index

Since then, new experimental work and proposals have been produced. In particular the MED POL work on biological indicators, the work of IOC/UNESCO WG on Benthic Indicators and the work of EMMA on eutrophication in the framework of the European Marine Strategy which brings together different approaches at the European level and at the level of Marine Conventions where the OSPAR approach has been considered as the basis for discussions. The present document was written and revised by Dr Giulio Izzo of ENEA taking into consideration the comments of other scientists expressed at various MED POL meetings.

2. Eutrophication monitoring and the Ecosystem Approach

MED POL Phase IV as approved by the 14th Ordinary Meeting of the Contracting Parties to the Barcelona Convention (Portoroz, December 2005) envisages that the ecosystem approach to the management of human activities that may affect the marine and coastal environment will be adopted and implemented by the countries. The short-term eutrophication monitoring strategy is a functional tool to manage nutrient loads from point and diffuse sources but does not really take into account the ecosystem sensitivity and indirect effects. With the new approach, monitoring programmes will have to be reviewed to integrate water quality monitoring and biological monitoring. Ecological indices integrating community structure and system functioning will gain more importance (de Jonge et al., 2006). These ideas should be promoted in the medium and long-term strategy for eutrophication.

3. Rationale

In the document UNEP(DEC)/MED WG.231/14 “Monitoring of Mediterranean Marine Eutrophication: Strategy, parameters and Indicators”, different definitions of eutrophication are discussed and finally the following is proposed:

“Eutrophication is an environmental perturbation caused by an **excess** in the rate of supply of organic matter “.

Organic matter mineralization is the key process in eutrophication. The main oxidising agents are oxygen, nitrate and sulphate. Oxygen is continuously supplied in the marine waters by the physical exchange between air and water and by the photosynthetic processes; its concentration in the water is about 8mg/l. During the night, of course, only physical exchange processes occur. Nitrate is present in a maximum concentration of about 1mg/l and could be supplied mainly by external inputs. Sulphate, in the seawater, is the most abundant oxidant: it is present in a concentration of about 2g/l. The three respiration processes are sequential in the sense that oxygen is always the first and if it is available the other two are hardly used. Oxygen and nitrate respiration do not produce stress factors in the aquatic ecosystem, but sulphate does, releasing reduced sulphur that is a strong stress factor on benthic community. Reduced sulphur compounds have many chemical and biological buffering systems that prevent their diffusion and toxicity into the ecosystem.

The word “**excess**” in the definition is important because it implicitly introduces the concept of the ecosystem threshold, which is the total mineralization capacity before H_2S that acts as a stress factor, is produced by the SO_4 respiration. Hydrogen sulphide is toxic and when it is not buffered it starts changing the biological assemblage of the benthos community; more sensitive species disappear and are substituted by the more resistant ones while the species diversity decreases. The redox state of the sediments changes, becoming reduced and in this physical-chemical environment the reactive phosphorus, that is insoluble in the oxidized environment, is released and becomes available. As more phosphorus becomes bio-available, eutrophication accelerates.

Eutrophication is an environmental perturbation and there is no “good” and “bad” eutrophication but it simply exists at different intensities within the process. Also, the use of the terms “natural” and “anthropogenic” eutrophication to note differences does not help to manage the phenomena, but increases confusion. There is no doubt that the main pressure that induces eutrophication is nutrient input. Generally, a natural nutrient input is not continuous in time but it is a single pulse phenomenon and the biogeochemical processes of the ecosystem, acting as negative feedback, are able to buffer and neutralize it in a relatively short time; denitrification and phosphorus precipitation are the most important processes.

EUTROPHICATION

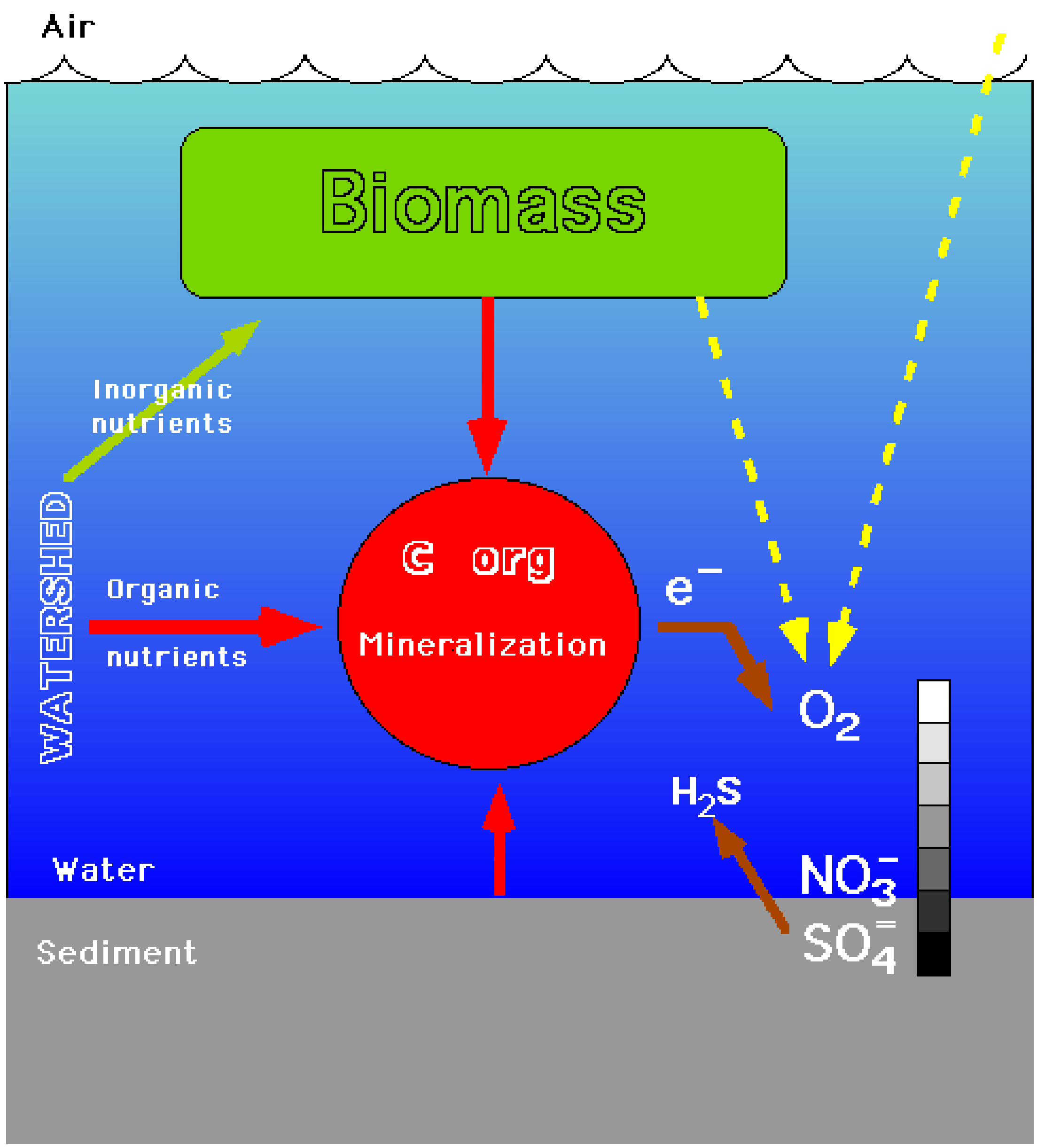
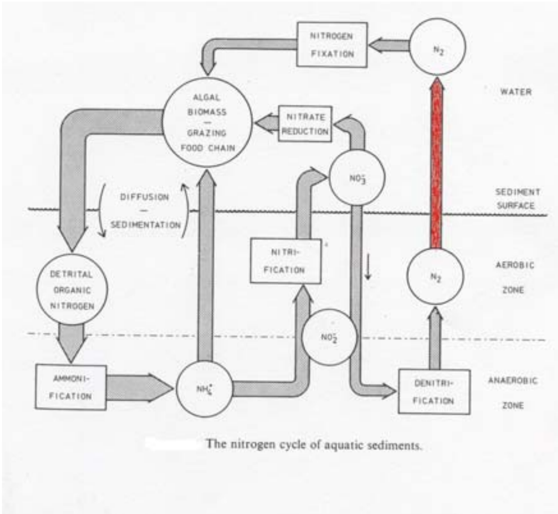


Fig 1. A general model of eutrophication



The nitrogen cycle of aquatic sediments.

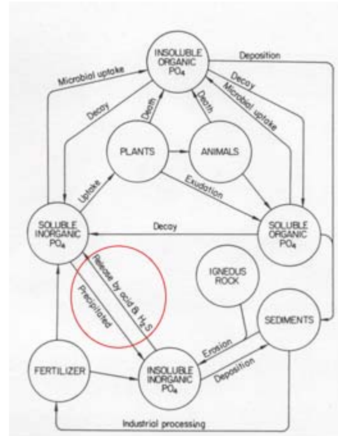


Fig. 2 Nitrogen and phosphorus cycles in aquatic sediments. Processes acting as negative feedback after nutrient input are shown in red.

Eutrophication occurs when there is a continuous input of nutrients, because the buffering mechanisms have a limited capacity and when this is overcome, the ecosystem begins to change its organization in terms of ecological structure and functions; the chemistry and biology of sediments also change.

Eutrophication effects in sediments follow a distribution that is dependent on the organic matter sedimentation process. This means that eutrophication's first effects have a different geographical distribution even within the same bay or coastline that is not necessarily related to the distance from the sources. Wherever in a coastal ecosystem eutrophication occurs, it is important to ascertain the hot spot zones (refer also to the Revision of Sediment Monitoring Strategy of MED POL, UNEP(DEC)/MED WG.282/Inf.5).

The perception of eutrophication is different if we look at marine ecosystems of different depths. In the shallow and medium depth ecosystems the benthic community could be directly affected. In deep waters, since a complete mineralization occurs in the water column, the bottom community is unlikely to be affected. The Black Sea is an exception still confirming the conceptual model of eutrophication (Fig.3) because its morphological characteristics (it is a semi-enclosed sea with long renewal time of water masses) and the rate of supply of organic matter affects the whole water column and bottom. A water column about 2000 m deep, contains no oxygen below 150 meters depth and contains high concentrations of hydrogen sulphide (H_2S) that diffuse in the water column and cause intensive nitrate reduction at intermediate depths.

This general model of eutrophication must be kept in mind when deciding the general monitoring strategy; parameters and state indicators.

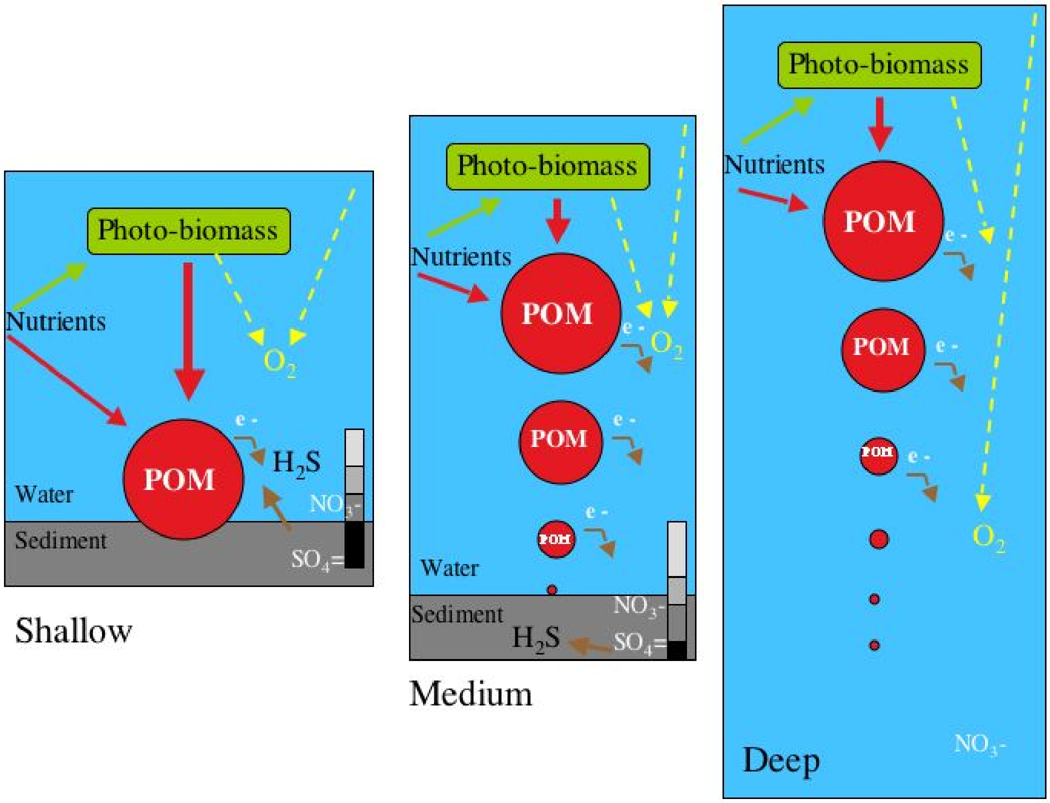


Fig. 3 General model of eutrophication with different depth of water column

4. Parameters to monitor

<u>4.1 In water</u>

4.1.1 Nutrients

Nutrient concentrations are the most used parameters in any monitoring programme. Although they are the major substances for the enhancement of eutrophication, the results of these analyses aren't always helpful in a state assessment, because these substances are not conservative. Nitrogen (basically inorganic nitrogen) and phosphorus in the sea environment have a very rapid cycle; they are transformed and utilized by microorganisms and enter in the food web. Consequently, the nutrient concentrations do not increase linearly with time as eutrophication grows. Seawater nutrient concentrations are always in the range of some hundred micrograms per litre for the total inorganic nitrogen and some tens of micrograms for reactive phosphorus. Nevertheless, nutrient monitoring gives important information.

- In general, in a yearly monitoring plan, nutrients show a characteristic trend; they are low during spring and summer when there is maximum primary productivity, and high during winter when photosynthetic organisms have their lowest growth. The winter maximum, which is one of the parameters adopted by OSPAR, gives a good picture of the total availability of nutrients, but it is often necessary to undertake frequent sampling in order to find the “winter peak”.

- The prevailing chemical form of nitrogen gives important information on the state of the environment. If nitrate is the main form, it means that the oxidative processes of the nitrogen cycle prevail on the reducing ones. Furthermore, nitrate is a very effective and ecosystem friendly oxidant for organic matter mineralization, because the main metabolite of this process is molecular nitrogen, that is lost in the air. The main nitrate reduction process is “denitrification”; this process inhibits sulphate reduction and can also oxidize sediments.
- Phosphorus is always the main eutrophication agent because there is no way for the marine ecosystem to produce it (like for example nitrogen fixation) and it tends to become unavailable in an oxidized environment after precipitation with iron hydroxides. Analysis of reactive phosphorus often results to zero or very close to it, even using very sensitive analytical methods, because the major portion of phosphorus is blocked in sediments (Fig. 2) and the bio-available quota is very rapidly utilised by photosynthetic organisms. Total phosphorus in water often gives a better picture of its availability.
- It is not rare in a monitoring programme to find high phosphate and ammonium together or low phosphate and high nitrate, because this depends on the general redox conditions of the environment.

4.1.2 Dissolved oxygen

Dissolved oxygen (DO) is a very effective parameter to assess the eutrophication state of a marine ecosystem, because it integrates the main biological processes, which are photosynthesis and respiration, that are contemporarily affected by external sources of nutrients. However, the sampling methods must be revised taking into account high diurnal variations of DO. DO concentration changes continuously during the day-night cycle with a characteristic harmonic curve. The classical one-time sampling during the day is not useful and can easily give a wrong assessment when comparing different points sampled in different times. On the contrary, the 24 hours monitoring of DO variation is very informative. The amplitude of the daily variation is a very good indicator of eutrophication state, because the oxygen balance is the simplest and clearest integrated parameter of the eutrophication effects. This is particularly true for shallow and medium depth environments, because the sediment respiration is the main cause of oxygen depletion. In case of a medium water depth environment, where there is an aphotic zone in the water column, the vertical profile of DO is useful too, but needs research and validation for its use.

The 24 hours DO cycle is without any doubt a very effective and simple method for the eutrophication state assessment, but needs a technological and scientific development. The monitoring instrument needed is an automatic DO probe with a waterproof data-logger. Up to day, the international market offers DO probes with these characteristics only in multiprobe apparatus that cost around 10,000-15,000 euros. Considering that, for a normal monitoring plan designed for a shallow ecosystem (e.g. a lagoon) at least 5-10 sampling points -for proper coverage of the whole area- must be followed at the same time, the cost of automatic instruments will jeopardise the common use of this method. It is known that efforts are made to develop cheaper instruments for a cost of about 1,000 euros each.

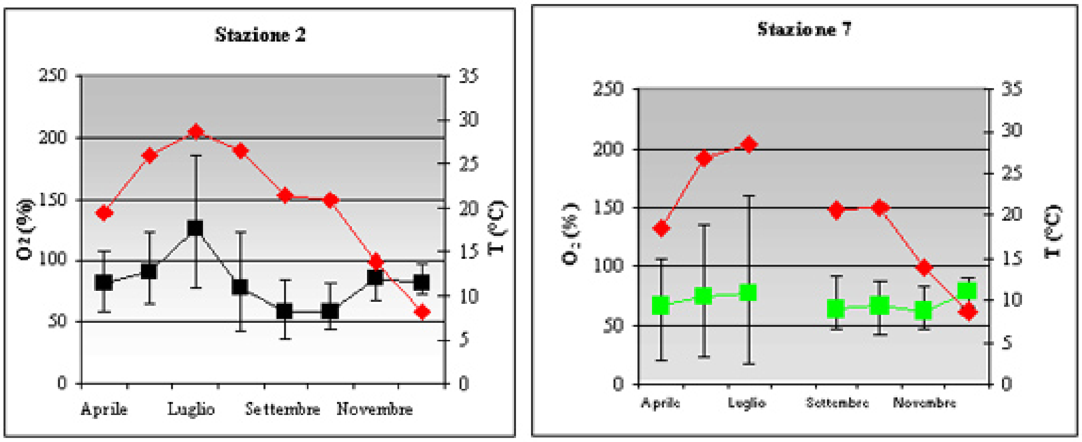


Fig. 5 Daily variation of dissolved oxygen in two different lagoons in Italy. Left, Caprolace lagoon and right Fogliano lagoon. The annual trend of temperature is in red, while the whiskers represent the 24 hours variation of DO. The wider variation registered in Fogliano lagoon indicates a major eutrophication

4.1.3 Plankton

The plankton community is the earliest to respond to changes in nutrient concentrations. Changes in plankton composition and production will in turn affect higher trophic levels of macroinvertebrates and fish. Plankton have generally short life cycles and rapid reproduction rates, making them valuable indicators of short-term impact, but their easy mobility due to winds, tides, and currents may negatively affect the accurate coupling with the source of impacts. This problem is amplified by the ability of some phytoplankton to synthesize atmospheric sources of nitrogen, thus confounding the identification of runoff sources of nutrients in estuaries and the resultant changes in the aquatic biota.
Many States routinely monitor chlorophyll "*a*" as part of water quality monitoring due to the ease and relatively low cost of analysis. Taxonomic identification of phytoplankton can be difficult and time-consuming. Competition by aquatic macrophytes, higher respiration rates, and increased grazing by zooplankton may counteract increased phytoplankton biomass resulting from nutrient enrichment. These reasons argue for investigating phytoplankton and zooplankton together as biological indicators. Phytoplankton can undergo blooms, the causes of which might be indeterminate, at varying frequencies.

4.2 In sediments

Eutrophication leaves a stable record of its main effects with changes in the chemistry and biology of the sediments; therefore sediments should be used as the key to a good assessment of the ecosystem state. It must be underlined that the distribution of these effects in the sediments is dependent on the sedimentation characteristics, which are often independent from the pollution source's distance. For this reason it is a priority of any monitoring plan to have a clear picture of the sedimentation characteristics of the area (UNEP(DEC)/MED WG.282/Inf.5).

4.2.1 Acid Volatile Sulphides (AVS)

AVS concentration in sediments is a good indicator of bacterial sulphate reduction and therefore of eutrophication state. They represent the chemical compounds generated by the reaction between reduced sulphur compounds and available cations in sediments. The bulk of these cations represent the chemical buffering capacity of the sediments. Many buffering systems exist against the reduced sulphur to prevent its diffusion and toxicity. The most important one is the chemical re-oxidation to sulphate, but when oxygen flow in sediments is slowed down for an increased biological demand, the reduced sulphur reacts with cations and increases the AVS concentration. When the sediment buffering capacity is saturated, the sulphide exerts its toxicity in the surrounding environment. Since the most abundant cation in sediment is iron, and iron content in sediments represents the chemical buffering capacity, the index AVS/Fe(II) (Viaroli et al., 2004) has been proposed as representative of this buffering capacity. This index has a potential utility in eutrophication work but needs further research.

4.2.2 Organic matter

The sediment organic matter (OM) accumulates as a result of the combined effect of increasing detritus production and low hydrodynamism that favours the increase of sedimentation rate. A high concentration of OM in the sediments is evidence of increasing eutrophication. Unfortunately, only the bio-available fraction of OM concurs in the eutrophication phenomena, and therefore it would be useful, for assessment purposes, to easily evaluate this fraction. The traditional and more distributed analytical methods evaluate total organic carbon (TOC) and not the bio-available fraction. TOC has been proven to be effective, while not a measure of causality, as a general screening-level indicator for evaluating the likelihood of reduced sediment quality and associated bio-effects over broad coastal areas receiving organic wastes and other pollutants from human activities (Hyland et al, 2005).

In the TOC there are, however, many fractions including small bio-available molecules and long refractory organic polymers. The analytical methods to evaluate the concentrations of different forms of organic matter are not easy and the assessment of OM bioavailability is even more complex. Recently, it has been proposed to use BPC (Biopolymeric Organic Carbon) as an index of trophic state in coastal environments (Dell'Anno et al, 2002). BPC is the sum of protein, carbohydrate and lipid fractions of organic carbon. This index has been tested for transitional waters and failed, but the ratio BPC/TOC resulted to be more effective. From this example it is evident that more research is needed to find an indicator of bioavailable OM in sediments.

4.2.3 Macrophytes

Aquatic macrophytes in estuarine and coastal marine waters may include vascular plants (e.g., seagrasses) and algae (e.g., sessile and drift). Vascular aquatic macrophytes are a vital resource because of their value as extensive primary producers in estuaries. They are a food source for waterfowl, a habitat and nursery area for commercially and recreationally important fish species, a protection against shoreline erosion, and a buffering mechanism for excessive nutrient loadings. The primary productivity observed for submerged aquatic vegetation (SAV) communities in estuaries is among the highest for any aquatic system. An important ecosystem function and buffering mechanism of seagrasses like *Cymodocea sp*. and *Zostera sp*. is the active transport of oxygen within the sediments through the root apparatus. This characteristic is the most important difference with seaweeds and also with some seagrasses like *Ruppia sp*. that have a superficial root apparatus.

The oxygen transport mechanism enhances the chemical buffering capacity for H_2S giving the seagrass dominated ecosystem a very high resistance to eutrophication. Excessive nutrient loadings lead to prolific phytoplankton and epiphytic macroalgal growth on seagrass, which out-compete the seagrass through shading; contemporaneous enrichment of labile organic matter in sediments overcomes aerobic mineralization and the chemical buffering capacity, cutting down the barriers for the diffusion of toxic H_2S. This process is evident by the decline of eelgrass and long life seaweeds in many coastal seas, like Baltic and Adriatic.

The presence or absence of macrophytes affects the entire estuarine or coastal marine biota, because of the combined high productivity and habitat function of this plant community. The main advantage of using aquatic macrophytes in a monitoring plan is that they are a sessile community. There is essentially no mobility to rooted vascular or holdfast-established algal plant communities, so expansion or contraction of seagrass beds can be readily measured as an environmental indicator; measurement of macrophyte community extent and relative density can be fairly easily accomplished by remote means, such as aerial photography, if the water is clear or shallow. Sampling frequency is reduced because of the relatively low community turnover compared to other biota such as benthic invertebrates or fish. Taxonomic identification in a given area is generally consistent and straightforward. The dominant species and its coverage are without any doubt relevant information for the assessment of environmental state and already some indices are focusing on this factor.

4.2.4 Macrozoobenthos

Benthic macro-invertebrates are appropriate assemblages for all biological assessments of water bodies, because they respond to water, sediment, and habitat qualities, are not very mobile, and consequently, integrate long-term changes in community structure and function. Benthic infauna is typically sedentary and therefore is most likely to respond to local environmental impacts; they are sensitive to disturbances of habitat such that the communities respond fairly quickly with changes in species composition and abundance. Individual macro-invertebrate species have sensitive life stages that respond to stress and integrate effects of short-term environmental variations, whereas community composition depends on long-term environmental conditions.

Some limitations of benthic infauna monitoring include: relatively few countries have the necessary, in house, taxonomic expertise to support extensive monitoring activities; current methods can distinguish severely impaired sites from those that are minimally impaired, however, it can be difficult to discriminate between slightly or moderately impaired areas, particularly in estuaries (due to their natural spatial and temporal variability). The cost and effort to sort, count, and identify benthic invertebrate samples can be significant, requiring tradeoffs between expenses and the desired level of confidence. In addition to taxonomic identification, benthic macro-invertebrate metrics may require knowledge of the feeding group to which a species belongs, for example, suspension feeders and deposit feeders. Among the zoobenthos indices proposed for quality assessment, some proved to be effective for coastal ecosystems while others for transitional waters. Many research groups are working to refine and validate these indices and it is reasonable to expect further improvements (Magni et al, 2005).

Conclusions

The conceptual framework of eutrophication mentioned above, suggests the introduction of new parameters and indicators more related to the benthic ecosystem and considered useful and consistent for assessing the eutrophication state. The international scientific community is at work to propose new and effective low cost parameters to be used in routine monitoring programmes. In particular, a strong stimulation for this exercise has been given by the requirements of WFD (Water Framework Directive) and its implementation. A large number of experimentations and discussions are going on, all around Europe, and it is reasonable to imagine that in a few years new effective indicators will be available. Up to now, there are only some converging proposals that need further implementation. The MED POL programme is contributing with its own expert groups in proposing and experimenting, on a pilot scale, new parameters for eutrophication assessment and management.

A summary of the proposal is provided in the following table, which is open for comments. In the table some common and new parameters are listed. With the symbol R are the recommended ones, which better fit with the conceptual model of eutrophication; with the symbol P are those, which, although relevant, need more experimentation.

Table 1: Parameters and indices used in assessment work

Matrix	Parameter	Proposed assessment INDEX	Environment			References						
Water			Shallow	Medium	Deep	1	2	3	4	5	6	7
Nutrients	N-Nitrate		U	U	U	x	x		x			
	N-Nitrite					x	x					
	N-Ammonium		U	U	U	x	x		x			
	P-Phosphate	TRIX	U	U	U	x	x		x			
	Total Phosphorus						x					
Dissolved oxygen	Punctual		U	U	U	x	x		x			
Phytoplankton	Chlorophyll “a”		U	U	U	x	x		x			
	Dominance		U	U	U	x	x		x			
	Remote sensing				U	x						
Dissolved oxygen	Daily variation		R	R	R							
Zooplankton	Biomass		P	P	P							x
Sediments	AVS	AVS/FE	R	R				x	x			
	OM (TOC, BPC, etc)	BPC, (BPC/TOC)	P	P				x				
Phytobenthos	Coverage Biomass	*Sensitive taxa e.g. Posidonia*, EEI, Benthos, Carlit	R	R					x	x	x	x
Zoobenthos	Macrobenthos	M-AMBI-BENTIX, S, H	R	R			x	x		x	x	x

U = already in use, R = recommended, P = potentially useful but not yet mature

1. Document UNEP(DEC)/MED WG.231/14 (http://195.97.36.231/acrobatfiles/03WG231_14_eng.pdf)
2. Document UNEP(DEC)/MED WG.231/17 (http://195.97.36.231/acrobatfiles/03WG231_17_eng.pdf)
3. IOC/UNESCO Workshop Report No.195 (Magni et al, 2005). (http://unesdoc.unesco.org/images/0013/001397/139719e.pdf)
4. Report of the Meeting of the Working Group on European Marine Monitoring and Assessment (EMMA) Copenhagen, 8 – 9 February 2005, 05/8/1, Annex 4, Appendix 1
5. Document UNEP(DEC)/MED WG.264/Inf.14 Marine Pollution Indicators: Fact Sheets (http://195.97.36.231/acrobatfiles/05WG264_Inf14_eng.pdf)
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Viaroli P., M. Bartoli, G. Giordani, P. Magni, D.T. Welsh (2004). Biogeochemical indicators as tools for assessing sediment quality/vulnerability in transitional aquatic ecosystems. Aquatic Conservation: Marine and Freshwater Ecosystems, S1: S19-S29.